

AD 746956

BRL MR 2195

BRL

AD

MEMORANDUM REPORT NO. 21-5

THE METAL ION CATALYZED OXIDATION OF HYDRAZINE WITH HYDROGEN PEROXIDE

by

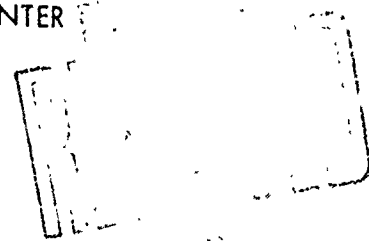
Lester P. Kuhn
Carl Wellman

May 1972

Approved for public release; distribution unlimited.

U.S. ARMY ABERDEEN RESEARCH AND DEVELOPMENT CENTER
BALLISTIC RESEARCH LABORATORIES
ABERDEEN PROVING GROUND, MARYLAND

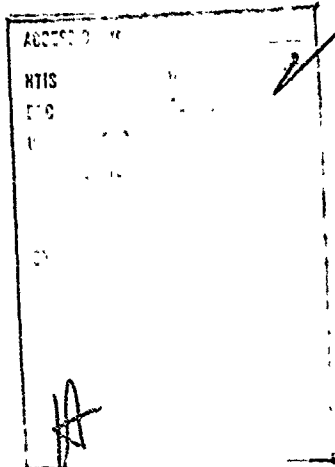
Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. Department of Commerce
Springfield, VA 22151



Destroy this report when it is no longer needed.
Do not return it to the originator.

Secondary distribution of this report by originating or
sponsoring activity is prohibited.

Additional copies of this report may be purchased from
the U.S. Department of Commerce, National Technical
Information Service, Springfield, Virginia 22151



The findings in this report are not to be construed as
an official Department of the Army position, unless
so designated by other authorized documents.

*The use of trade names or manufacturers' names in this report
does not constitute indorsement of any commercial product.*

BALLISTIC RESEARCH LABORATORIES

MEMORANDUM REPORT NO. 2195

MAY 1972

THE METAL ION CATALYZED OXIDATION OF HYDRAZINE WITH HYDROGEN PEROXIDE

Lester P. Kuhn

Carl Wellman

Interior Ballistics Laboratory

Approved for public release; distribution unlimited.

RDTE Project No. 1T061101A91A

ABERDEEN PROVING GROUND, MARYLAND

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) U. S. Army Aberdeen Research & Development Center U.S. Army Ballistic Research Laboratories Aberdeen Proving Ground, MD 21005		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP N/A
3. REPORT TITLE THE METAL ION CATALYZED OXIDATION OF HYDRAZINE WITH HYDROGEN PEROXIDE		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)		
5. AUTHOR(S) (First name, middle initial, last name) Kuhn, Lester P. Wellman, Carl R.		
6. REPORT DATE May 1972	7a. TOTAL NO. OF PAGES 20	7b. NO. OF REFS 7
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. IT061101A91A		BRL Memorandum Report No. 2195
c.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.		
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY U.S. Army Materiel Command Washington, DC 20315
13. ABSTRACT Hydrazine reacts readily with hydrogen peroxide in aqueous solution to yield nitrogen and water. The rate of the reaction as measured by the rate of nitrogen evolution is quite erratic. Using a solution that is 0.4 molar in hydrogen peroxide and 0.2 molar in hydrazine and the temperature at 25°C, the initial rate of the reaction varied from 0.6 to 0.8 ml per second. The reaction was found to be first order in peroxide and zero order in hydrazine. The rate of the reaction depends upon the history of the water which is used as solvent. Tap water gives the slowest rate. Water that has been distilled in a Barnstead metal still (tin plated) gives the fastest rate, and water that has been distilled first in the Barnstead still and then in a Pyrex still gives a rate which is intermediate between the first two. The addition of very small amounts of ethylene diamine tetraacetic acid, EDTA completely suppresses the reaction. The experimental results are compatible with a mechanism in which the hydrazine forms a complex with trace metals which are present inadvertently in the reaction mixture. The complex reacts with the peroxide in a rate determining step to give products. The reaction is inhibited by EDTA because the EDTA forms a very stable complex with the metal ions which is unreactive to peroxide.		

DD FORM 1473

REPLACES DD FORM 1075, 1 JAN 60, WHICH IS OBSOLETE FOR ARMY USE.

1

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Hydrazine Hydrogen Peroxide Gas Generator Trace Metal Catalysis						

BALLISTIC RESEARCH LABORATORIES

MEMORANDUM REPORT NO. 2195

LPKuhn/CRWellman/cs
Aberdeen Proving Ground, Md.
May 1972

THE METAL ION CATALYZED OXIDATION OF HYDRAZINE WITH HYDROGEN PEROXIDE

ABSTRACT

Hydrazine reacts readily with hydrogen peroxide in aqueous solution to yield nitrogen and water. The rate of the reaction as measured by the rate of nitrogen evolution is quite erratic. Using a solution that is 0.4 molar in hydrogen peroxide and 0.2 molar in hydrazine and the temperature at 25°C, the initial rate of the reaction varied from 0.6 to 0.8 ml per second. The reaction was found to be first order in peroxide and zero order in hydrazine. The rate of the reaction depends upon the history of the water which is used as solvent. Tap water gives the slowest rate. Water that has been distilled in a Barnstead metal still (tin plated) gives the fastest rate, and water that has been distilled first in the Barnstead still and then in a Pyrex still gives a rate which is intermediate between the first two. The addition of very small amounts of ethylene diamine tetraacetic acid, EDTA, completely suppresses the reaction. The experimental results

are compatible with a mechanism in which the hydrazine forms a complex with trace metals which are present inadvertently in the reaction mixture. The complex reacts with the peroxide in a rate determining step to give products. The reaction is inhibited by EDTA because the EDTA forms a very stable complex with the metal ions which is unreactive to peroxide.

TABLE OF CONTENTS

	Page
ABSTRACT.	3
I. INTRODUCTION.	7
II. EXPERIMENTAL PROCEDURE	7
III. RESULTS	8
IV. DISCUSSION.	11
V. CONCLUSION.	13
REFERENCES.	15
DISTRIBUTION LIST	17

I. INTRODUCTION

Hydrazine and its derivatives are used quite widely as the fuel in liquid rocket and gun propellants. They are also used in gas generators. A considerable effort has been expended in the search for catalysts for this application.^{1*} For some time now we have been studying the catalytic oxidation of hydrazine with various oxidizers. Some of this work has been published.² In the course of this work we found that hydrazine reacts readily with hydrogen peroxide in aqueous solution to yield nitrogen and water. A search of the literature revealed that this reaction had already been studied by Alvin Gordon in 1949.³ A comparison of his data with ours revealed that we were getting reaction rates which were much faster than his and so we decided to re-examine this reaction. The results of this work are contained in this report.

II. EXPERIMENTAL PROCEDURE

Reagents. Anhydrous hydrazine, 97% was obtained from Matheson, Coleman and Bell, Norwood, Ohio. An approximately 4 molar stock solution was prepared with cold distilled water. The molarity was determined by titration with iodate.⁴ Hydrogen peroxide, 97% was obtained from the Becco Chemical Division of the Food Machinery and Chemical Corporation, Buffalo, N.Y. An approximately 4 molar stock solution was prepared. Both stock solutions were stored in the refrigerator when not in use.

Procedure. The reactions were carried out in a 125 ml Erlenmeyer flask fitted with a side arm that led to a gas bubbler and a gas burette for collecting and measuring the gas evolved over mercury. The neck of the flask was fitted with a silicone rubber stopper which contained a 25 ml burette and inlet tube for the introduction of

*References are listed on page 15.

helium gas. The flask was held in a thermostatted bath at 25°C, the vigorous stirring was maintained with a Teflon coated magnetic stirring bar. The desired amount of hydrogen peroxide stock solution was added from a pipette to a volume of distilled water contained in the reaction flask. The volume of water was such that the total volume of solution after everything was added was 50 ml. The rubber stopper was firmly inserted in the neck of the flask and the flask was placed in the constant temperature bath and the apparatus was flushed well with helium for ten minutes. The flow of helium was stopped and the desired amount of hydrazine stock solution was introduced through the burette. The magnetic stirrer and timer were started simultaneously and the reaction product gas collected in the 100 ml gas burette. The gas was maintained at atmospheric pressure with the leveling bulb. The time elapsed for every 10 ml of gas collected was recorded.

III. RESULTS

The rate of the reaction was readily followed by measuring the rate of gas (nitrogen) evolution. This was done by plotting the volume of gas evolved as a function of time and measuring the slope of the line at time equals zero. A disquieting feature of this reaction is the irreproducibility of the rate. A series of runs were made in which the initial concentration of reactants was kept constant, hydrogen peroxide, 0.4 molar, hydrazine, 0.2 molar, temperature at 25°C. These experiments were carried out over a period of several months. The observed initial rates are shown in Table I.

TABLE I

Initial Rate of Reaction of Hydrogen Peroxide (0.4 molar)
with Hydrazine (0.2 molar) at 25°C. Total Volume = 50ml

Run No.	Initial Rate in ml/sec.
1	.81
2	.66
3	.61
4	.68
5	.68
6	.80
7	.68
8	.62
9	.57
10	.63
11	.74
12	.71
13	.80

Thus we see that the initial rate of the reaction varies from 0.57 to 0.81 ml/sec although the reaction conditions were kept constant as far as we were aware.

The order of the reaction with respect to each reactant was determined by making a series of experiments in which the concentration of hydrogen peroxide was kept constant and the concentration of hydrazine was varied by a factor of four. Then the hydrazine was kept constant and the concentration of hydrogen peroxide was varied. Because of the erratic nature of the rates, each rate was measured at least four times and an average value was taken. In this manner we were able to get meaningful values for the reaction rates which are shown in the last column of Table II.

TABLE II
Determination of the Order of the Reaction Between Hydrogen
Peroxide and Hydrazine

Hydrazine (Molarity)	Hydrogen Peroxide (Molarity)	Rate ml/sec
0.1	0.4	0.60
0.2	0.4	0.70
0.4	0.4	0.60
0.2	0.2	0.35
0.2	0.4	0.70
0.2	0.8	1.40
0.1	0.2	0.38
0.2	0.4	0.70
0.4	0.8	1.40

When the hydrogen peroxide is kept constant and the hydrazine concentration is varied, the rate remains constant, indicating that the reaction is zero order in hydrazine. When the concentration of hydrazine is kept constant and the concentration of peroxide is varied, the rate varies. The rate is proportional to the concentration indicating that the reaction is first order in peroxide. When both hydrogen peroxide and hydrazine are varied the rate is again first order in peroxide and zero order in hydrazine.

Another unusual feature of this reaction is that the rate of the reaction depends upon the history of the water that is used as the reaction solvent. Keeping the initial conditions constant but varying only the treatment of the water we find that the reaction goes slowest in tap water, fastest in water that has been once distilled in a Barnstead metal still (tin plated), and at an intermediate rate in water that has been distilled once in a Barnstead still and a second time in a Pyrex still. The results are shown in Table III.

TABLE III

Effect of the History of Three Samples of Water
Upon the Initial Reaction Rate; Hydrogen Peroxide
0.4 Molar, Hydrazine 0.2 Molar, Volume 50 ml, T. 25°C.

<u>History of Water Sample</u>	<u>Initial Rate ml/sec</u>
1. Tap Water	0.04
2. Distilled once in a Barnstead metal still	0.70
3. Distilled once in a metal still and once in a Pyrex still.	0.08

The effect of EDTA, ethylene diamine tetraacetic acid, on each of the solutions shown in Table III were studied. In each case a .02 molar solution of EDTA completely inhibited the reaction.

IV. DISCUSSION

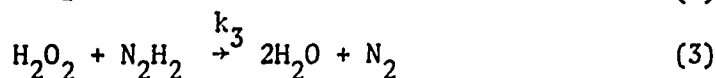
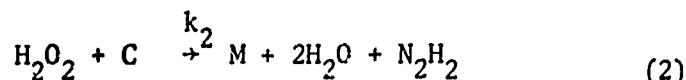
A clue that the mechanism of this reaction involves trace metal catalysis is provided by the statement of Edwards⁵, "The best evidence that trace metals are involved in a reaction mechanism is an unusual rate law (first order in peroxide but zero order in reducing agent) coupled with erratic rate constants." This is exactly the situation that fits our data.

Let us assume that there are traces of metal ions, M, inadvertently present in the reaction mixture and that these ions can form a complex, C, with hydrazine,

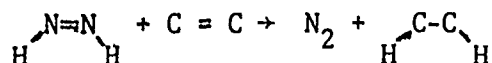


$$K = \frac{(C)}{(M)(N_2H_4)}$$

The complex reacts with hydrogen peroxide in a rate-determining step to give water, diimide (N_2H_2) and metal ion. The diimide reacts very rapidly with hydrogen peroxide to yield nitrogen and water:



The intermediacy of diimide is not required by the kinetics but the presence of diimide has been inferred from experiments in which the reaction of hydrazine with hydrogen peroxide was carried out in the presence of olefins and trace amounts of copper ions. Cis hydrogenation of the double bond takes place in high yield⁶.



Let us now derive the rate equation for the above mechanism. From equation (1), $(C) = K(M)(N_2H_4)$ and $(M) = \frac{(C)}{K(N_2H_4)}$. The total metal ion concentration, $(M)_T$ is the sum of the free metal ion concentration (M) plus the concentration of complex, (C)

$$(M)_T = (M) + (C) = (M) + K(M)(N_2H_4) = (M)(1 + K(N_2H_4)).$$

Assuming that the second step is slow and rate-determining, the rate equation is $\text{rate} = dN_2/dt = k_2(C)(H_2O_2) = k_2(H_2O_2)K(M)(N_2H_4)$

but

$$(M) = \frac{(M)_T}{1 + K(N_2H_4)} \quad \text{therefore,}$$

$$\text{rate} = \frac{k_2(H_2O_2)K(N_2H_4)(M)_T}{1 + K(N_2H_4)}$$

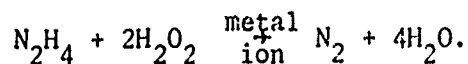
If we assume that $K(N_2H_4) \gg 1$ then the rate equation is

$$\text{rate} = k_2 (H_2O_2) (M)_T$$

Thus we see that the proposed mechanism shown above requires that the reaction be zero order in hydrazine and first order in hydrogen peroxide which is in agreement with experiment. The reaction should also be first order in metal ion concentration. We could not verify this since we had no control over the metal ion concentration. The reason that the rate measurements were erratic, as shown in Table I, was due to the fact that the concentration of metal ions was not kept constant. The effect of different treatment of the water on the reaction rate shown in Table III can be explained by attributing the effect to a difference in concentration of trace metal ions. Distillation in a Barnstead metal still produces water in which the rate goes fastest. This must be due to the picking up of metal ions by the water either during distillation or during storage. Distillation in a Pyrex still produces water in which the reaction is much slower indicating that some metal ions were removed but not all. The ability of EDTA at low concentrations to completely suppress the reaction provides further evidence that the reaction is catalyzed by traces of metal ions.⁷ EDTA has the ability to form very stable complexes with metal ions. These complexes are not attacked by hydrogen peroxide and so the reaction is suppressed.⁷

V. CONCLUSION

Hydrogen peroxide has been found to oxidize hydrazine at room temperature in water solution,



Metal ions must be present but only trace amounts are necessary. The data are consistent with a mechanism in which the hydrazine forms a

complex with metal ions and this complex reacts with hydrogen peroxide in a slow rate-determining step. Although metal ions were not introduced intentionally, they were present in sufficient quantity in distilled water to allow the reaction to occur readily. On the basis of the results found in this work, we may recommend that in gas generators based on hydrazine, reaction rates may be increased by the addition of metal ions and may be decreased by the addition of EDTA. Similar effects may also be obtained in liquid gun and rocket propellants based on hydrazine. It is of interest to speculate about how the metal ion catalyzes the reaction. A possible explanation is that the positively charged metal-hydrazine complex will form the metal-hydrazine-peroxide transition state easier than the neutral hydrazine. In other words, the metal-hydrazine complex is more electrophilic than the uncomplexed hydrazine.

ACKNOWLEDGEMENT

We thank Professor John O. Edwards of Brown University and Dr. Richard Ward of Ballistic Research Laboratories, for many helpful suggestions and advice.

REFERENCES

1. (a) D. R. Poole, Development of Low Temperature Gas Generator Technology AFRPL-TR- 68-77 June 1968. (b) D. Huxtable, P. Rice, and O. Smith, Hydrazine Catalyst Evaluation AFRPL-TR-70-107. Nov. 1970
2. L. Kuhn, Journ. Amer. Chem. Soc., 73, 1510 (1951)
3. A. Gordon, "Third Symposium on Combustion" Williams and Wilkins Co. Baltimore, Md. 1949 P. 493.
4. R. Penneman and L. Audrieth, Anal. Chem., 20, 1058 (1948)
5. J. O. Edwards, "Inorganic Reaction Mechanisms" W. A. Benjamin Inc., N. Y. 1965 p. 74.
6. E. Corey, W. Mock, and D. Pasto, Tetrahedron Letters, 347 (1961).
7. E. Koubek, M. Haggett, C. Battaglia, K. Ibne-Rasa, H. Pyun, and J. Edwards, J. Amer. Chem Soc., 85, 2263 (1963).